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Procedia Engineering 87 (2014) 1609 – 1612

**Procedia
Engineering**www.elsevier.com/locate/procedia

EUROSENSORS 2014, the XXVIII edition of the conference series

Correlations phonon spectrum-sensitivity in metal-oxide gas sensors

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Abstract

We show that the sensitivity of metal-oxide gas sensors to a given gas peaks at temperatures which correspond to specific oxide phonon energies. It indicates that atomic vibrations contribute to the sensing mechanism and explains the dependence of the sensitivity on the exposed facet. In addition, the signature of the molecular vibrations in sensitivity is reported. Lattice anharmonicity as ingredient in shaping the sensitivity peak is introduced. The existence of a resonant charge transfer when the phonon frequency matches a molecular vibration one is brought to the fore.

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Peer-review under responsibility of the scientific committee of Eurosensors 2014

Keywords: phonon, sensitivity, metal-oxide, gas, sensor; molecular vibrations, anharmonicity.

1. Introduction

The sensitivity of metal-oxide gas sensors exhibits peaks located at temperatures which depend on oxide and target molecule. The origin of these maxima is a longstanding conundrum in this sensor technology. The mechanism widely accepted relies on the adsorption-desorption of both target molecule and oxygen species [1] from or diffusion [2] into the sensing layer. In this context, it was reported that sensitivity vs. temperature depends on the exposed crystallographic facet [3]. But a facet-dependent sensitivity hints to a contribution of the substrate atoms in the microscopic mechanism of sensing. That because their thermal vibration frequencies/energies are specific to the symmetry directions/points in the crystal and the associated crystallographic facets. At a given temperature, the atomic vibrations on a given facet could favor the adsorption-desorption of some gas molecules and/or the charge transfer, therefore the peak in sensitivity vs. temperature, $S(T)$. On the other hand, in the frequency domain, each line in the oxide phonon spectrum is the signature of the atomic vibrations at a given point of symmetry. If correct,

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this observation suggests a possible correlation between sensitivity peaks and the phonon spectrum of the sensing material. In this work, we show that this correlation exists. To this purpose, existing experimental data of sensitivity for CeO_2 , SnO_2 and ZnO in different gases and volatile organic compounds atmosphere were compared with Raman and/or infrared spectra of the oxide, respectively. To correlate the temperature scale with the phonon energy one (in cm^{-1}), the absolute temperature was multiplied with the Boltzmann constant ($8.617 \times 10^{-5} \text{ eV/K}$) and the resulted energy (in meV) was multiplied with 8.06 cm^{-1} (equivalent of 1 meV in wavenumbers).

2. Results and discussion

CeO_2 has a single allowed zone-center (Raman) mode at 465 cm^{-1} [4]. It has been reported that $S(T)$ of CeO_2 for CO peaks at 390°C (460.5 cm^{-1}) [5], while for NO, CeO_2 shows a peak at 400°C (467.4 cm^{-1}) [6]. Fig. 1 shows that both CO and NO sensitivity peaks correlate well with the CeO_2 Raman line. Since this mode is due to the “symmetric breathing of the O atoms around each cation” [7], this correlation points to the lattice oxygen participation in the sensing mechanism. For both NO and acetone, Bene *et al.* [6] observed enhanced sensitivity when the whole system (sensor and molecule) was oven-heated. They concluded that the effect is due to thermal activation of the molecules.

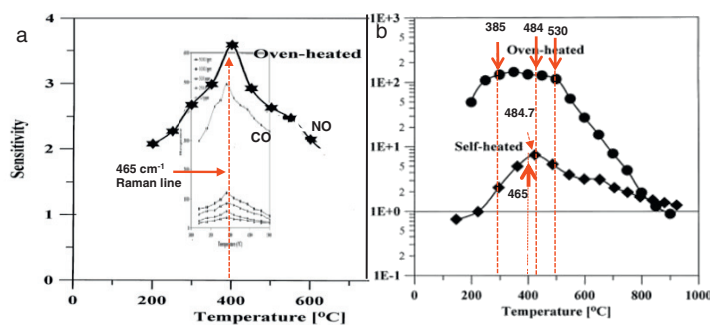


Fig. 1. (a) Comparison between $S(T)$ of CeO_2 for CO [5] and NO (stars)[6] and the Raman line (red curve) of the CeO_2 single crystal [1]; (b) Bene *et al.*'s data [6] for $S(T)$ of CeO_2 to acetone; downward oriented arrows indicate the molecular vibration energies (in cm^{-1}) of acetone.

It means that the charge transfer would be more efficient when some molecular vibration modes are excited by absorption of infrared radiation. This observation suggests that not only the atomic motion in the oxide but also the molecular vibrations could be involved in the sensing mechanism. The fingerprint of molecular vibrations can be uncovered if one investigates Bene and coworkers' data for acetone (Fig. 1b). When oven-heated, the sensitivity features a plateau between about 250 and 500°C . The equivalent temperatures of the four lowest infrared vibration frequencies (109 cm^{-1} , 385 cm^{-1} , 484 cm^{-1} and 530 cm^{-1} [8]) of the gaseous acetone are: -116°C , 281°C , 424°C and 490°C , respectively. The last three temperatures, indicated with downward-oriented arrows (Fig. 1b) are located on and delimit the plateau, a strong argument in favor of the molecular activation as a source of better charge transfer. The increased sensitivity observed when target molecule is activated raises the question whether the molecular activation is a *sine qua non* condition for the charge transfer, in general. When self-heated, the sensor features a peak at 425°C (484.7 cm^{-1}), a frequency in agreement with the 484 cm^{-1} vibration mode of acetone. It would indicate that acetone molecule is activated even when the sensor is self-heated. Since no first order CeO_2 phonon energy fitted the 484 cm^{-1} mode, we found that a second order combination of a transverse acoustic phonon (TA at 183 cm^{-1}) with a transverse optical one (TO at 300 cm^{-1}), both at the X point of symmetry, gives 483 cm^{-1} [9], a value close to 484 cm^{-1} acetone mode. This combination of atomic motions could be the one which selectively activates the molecules. However, its frequency can be slightly red-shifted by lattice anharmonicity,

Attempting to establish such correlations for SnO_2 proved to be quite difficult because the phonon spectra of this oxide considerably depend on its preparation, annealing temperature, morphology, etc. [10]. The SnO_2 sensitivity curves for CO, ethanol and CH_4 of Licznarski [11], shown in Fig. 2a, feature peaks at 425°C , 475°C and 625°C , respectively. Their equivalents in wavenumbers are 484.8 cm^{-1} , 519.5 cm^{-1} and 623.8 cm^{-1} , respectively. In Fig. 2a,

the sensitivity data are compared with the infrared spectrum, both complete and deconvoluted, of a SnO_2 film annealed at 450°C from Dieguez *et al.* [10]. The deconvolution peaks are located at 473cm^{-1} , 523cm^{-1} , 613cm^{-1} and 572cm^{-1} . The first three phonon bands correlate reasonably well with the position of the sensitivity maxima. The peak at 572cm^{-1} seems to be correlated with a singularity in the CO sensitivity at 550°C (571.6cm^{-1}).

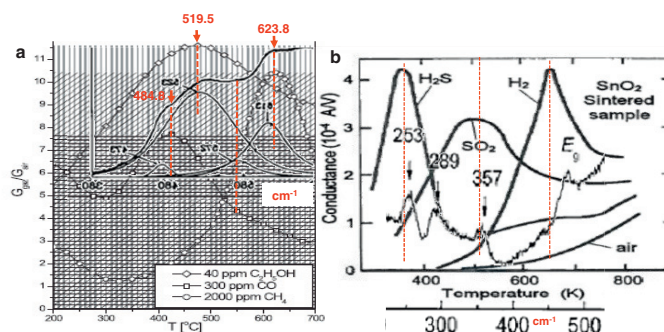


Fig. 2. (a) Comparison between $S(T)$ of SnO_2 for ethanol, CO, and methane (Licznarski [11]) and the FTIR spectrum of SnO_2 [10]. The downward-oriented arrows and the associated numbers indicate the energy (in wavenumbers) of the sensitivity peaks; (b) Pijolat's data [12] vs. SnO_2 Raman spectrum from [13]; red lines and numbers (cm^{-1}) indicate the position of the conductance peaks and the Raman lines, respectively.

Inherently, there is some uncertainty in assigning a phonon mode to a sensitivity peak. In fact, a perfect fit should not be expected as long as the phonon line does not is not measured at the temperature of sensing. In this respect, in Fig. 2b, Pijolat's data [12] for SnO_2 conductivity in H_2S , SO_2 and H_2 atmosphere is compared with the Raman spectrum from Chen *et al.* [13]. Although the H_2S peak, for instance, is in good agreement with the 253cm^{-1} line, its position is at a smaller frequency than the spectral line. The difference (within 1-3%) is due to lattice anharmonicity.

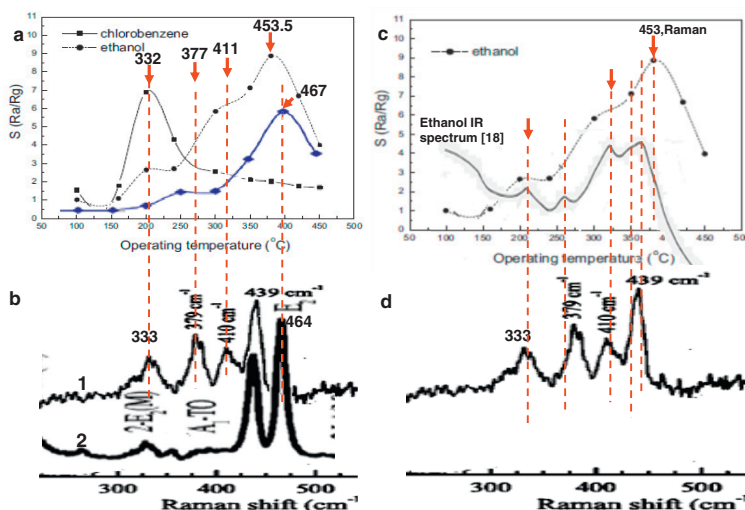


Fig. 3. (a) $S(T)$ of ZnO for chlorobenzene, ethanol [14] and NH_3 [15] vs. (b) Raman spectra of bulk ZnO : 1-16 and 2-17; numbers nearby red arrows are energies of the sensitivity peaks in cm^{-1} ; red lines connect sensing peaks with Raman bands; (c) $S(T)$ [14] vs. gaseous ethanol infrared spectrum [18]; (d) ZnO Raman spectrum [16]; red arrows/lines denote the sensitivity peaks/ethanol infrared bands.

The sensitivity curves of ZnO for chlorobenzene, ethanol [14] and NH_3 [15] are compared with two ZnO bulk Raman spectra [16, 17] in Figs. 3a,b. $S(T)$ peaks at 332, 377, 411 and 467cm^{-1} correlate well with different Raman bands. The 333cm^{-1} band corresponds to a combination of two phonons ($2E_2$) at the M point of symmetry, therefore

the facet responsible for the chlorobenzene sensing peak can be found. Similarly, the facets responsible for all sensitivity peaks can be identified for the examples given here. The ethanol peak at 453.5cm^{-1} has no correspondent in the Raman spectra but it is in agreement with a 453cm^{-1} ethanol Raman band (Fig. 3c). As Figs. 3c and d show, the other two singularities in the sensitivity occur when a molecular vibration band is aligned with a specific atomic vibration band in the oxide. The main, fundamental cause is the infrared shift due to oxide matrix anharmonicity but a blue/red shift of the molecular mode due to surface coupling can also contribute, or both of them. Apparently, when a “travelling” phonon frequency matches a molecular vibration one, a kind of (stochastically) resonant or coherent (?) charge transfer occurs. This state is progressively destroyed once the anharmonicity goes up with temperature and the oxide phonon frequency gets lower. For ZnO with different morphologies [3], the ethanol peak observed at 350°C (432.7cm^{-1}) is 1.43% less than the 439cm^{-1} vibration frequency of the ZnO lattice oxygen (Fig. 3b) and 1.33% higher than an ethanol band at 427cm^{-1} [18] (Fig. 3c). A red shift of 6.3cm^{-1} of the lattice oxygen frequency, corroborated with a blue shift of the ethanol mode, could explain the occurrence of the sensitivity peak.

3. Conclusion

It has been found that the sensitivity peaks of CeO_2 , SnO_2 and ZnO to different gases occur at the specific oxide phonon energies. It validates the hypothesis that thermal atomic motion contributes to the sensing mechanism. The fingerprints of the molecular vibration in sensing were observed and the role of the lattice anharmonicity was revealed. A model to explain the sensitivity peaks was tentatively proposed.

Acknowledgements

This work has been partially funded by the EU FP7 SOI-HITS project (Smart Silicon-on-Insulator Sensing Systems Operating at High Temperature - www.soi-hits.eu).

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